Technical Comments Draft Streamlined Copper Water-Effect Ratio Study Report Two Bayou Creek, Arkansas

Prepared for Shumaker Public Service Corporation, East Camden, Arkansas Highland Industrial Park Wastewater Treatment Plant NPDES No. AR0034363

2/22/2008

The Environmental Protection Agency (EPA) Region 6 is pleased to have the opportunity to provide a technical review of the *Draft Streamlined Copper Water-Effect Ratio Study Report* for Two Bayou Creek located within the Gulf Coastal ecoregion and Ouachita River basin of Arkansas. EPA received the draft report on January 30, 2008, and offers the general and specific comments on the draft report as provided below, in addition to any comments that the Arkansas Department of Environmental Quality (ADEQ) may have. Overall, EPA found the draft report to be well-written and well-organized. However, consideration of the technical comments provided below is encouraged in both selecting the final water-effect ratio (WER) to be used in establishing site-specific copper criteria for Two Bayou Creek and in enhancing the clarity of the final report.

GENERAL COMMENTS

Comment 1, Clarification Requested on Upstream Sampling Site Location. Figures 2-1 and 2-2 in the draft WER study report provide a schematic drawing and map of the Shumaker facility and its discharge to Two Bayou Creek (the NPDES permit for this facility describes a direct discharge to Two Bayou Creek), as well as the effluent and upstream sampling site locations utilized in collecting water samples for the WER study. Clarification is requested about whether the upstream sampling site is located on Two Bayou Creek itself or on a tributary to Two Bayou Creek. From the figures in the draft report, it appears that the upstream sampling site for the WER study was located on a tributary to Two Bayou Creek that enters Two Bayou Creek downstream of the Shumaker facility. While it appears that the sampling was conducted on this tributary upstream of its confluence with Two Bayou Creek (i.e., outside the influence of the Shumaker discharge), clarification is requested as to why this location (on what appears to be a tributary to Two Bayou Creek) was chosen instead of a location on Two Bayou Creek itself above the Shumaker discharge.

EPA's rationale for seeking these clarifications: Assuming that the Two Bayou Creek flow measurements were taken at the upstream sampling site as shown in Figures 2-1 and 2-2 of the draft report, EPA is concerned that flows (and, therefore, potentially water chemistry) at the upstream sampling site location may not be representative of conditions occurring in Two Bayou Creek itself upstream of the facility's discharge. For example, EPA noted that the NPDES permit for Shumaker's discharge (AR0034363) provides a 7Q10 background low flow of 0.3 cubic feet per second (cfs) for Two Bayou Creek. However, measurements during the first WER study event provide a flow of 16 cfs for Two Bayou Creek, despite the lack of rainfall for several

days prior to the sampling event. If the upstream water sample is not representative of true upstream conditions in Two Bayou Creek above the facility's discharge, then the simulated downstream water created for the WER study may not be representative of actual conditions in Two Bayou Creek at the edge of the facility's mixing zone. This could, in turn, lead to the establishment of a WER that is not representative of true site conditions. Responses to the two clarifications requested above should help EPA in determining whether the upstream water samples collected for the WER study were representative of true site conditions.

Comment 2, Notation Concerning Individual and Final WER Calculations. The draft WER study report provides a final dissolved copper WER of 15.36, based upon the geometric mean of two dissolved WERs derived from individual WER test events. The first WER test was conducted in January 2007 and produced a WER of 11.5. The second WER test was conducted in February 2007 and produced a WER of 20.54. However, please note that EPA calculated slightly different dissolved copper WERs for the two tests (11.8717 and 20.2966) using time-weighted average measured dissolved copper concentrations (as recommended in EPA's 1994 Interim Guidance on Determination and Use of Water-Effect Ratios for Metals (1994 interim WER guidance, see page 59) and Ceriodaphnia dubia mortality values provided in the draft report. Please refer to comments #11(b), 12, 15(b) and 16 below, for a more detailed discussion of EPA's calculations, as well as EPA's recommendations for addressing this issue.

Comment 3, Recommendation to Eliminate the Second Study Event WER from the Final WER Determination. Apart from comment #1 above, information presented in the draft report also indicates that the conditions under which samples were collected during the second WER test may not be representative of (1) normal plant operating conditions and (2) base-flow conditions in Two Bayou Creek. These conditions may have contributed to the second WER study event's large WER value of 20.2966, which is almost twice that determined from the first WER study event.

Page 4-4 to 4-5 of the draft report states,

"Shumaker reported TSS as 5 mg/L and American Interplex reported the TSS as 16 mg/L. The average daily maximum is 6.171 mg/L and the range is 2 to 9 mg/L."

The reported 16 mg/L TSS concentration is over two and a half times greater than the average daily maximum value and over three and a half times greater than the monthly average value reported in Table 1-1 of the draft WER study report. This indicates that TSS concentrations in the effluent sample collected in the second WER test event may not have been representative of normal conditions.

Further, page 2-2 of the draft report provides that, "1.08 inches of rain accumulated for the days of the [second] study event." The discharge rate for Two Bayou Creek (upstream of plant's discharge) during the second study sampling event (reported on page 4-4 of the draft report as 161 cfs or 104 million gallons per day (mgd)) confirms the presence of elevated flows in Two Bayou Creek. The discharge rate during the second study sampling event was approximately ten times higher than during the first study sampling event (reported as 16 cfs or 10 mgd).

Given the above considerations, EPA strongly recommends that the final WER be based only upon the WER determined from the first WER study event (final WER = 11.8717). Information provided on page 34 of EPA's streamlined WER guidance, as well as information presented in pages 10-12 of EPA's 1994 interim WER guidance, support the use of this approach. Furthermore, in reviewing the draft study report, EPA utilized a final WER value of 11.8717 to conduct reasonable potential calculations for copper (using assumptions provided in the factsheet associated with Shumaker's NPDES permit effective on September 1, 2003). From these calculations, it appears that use of a final WER of 11.8717 in deriving site-specific copper criteria for Two Bayou Creek should result in a determination of no reasonable potential for impairment of the aquatic life use due to copper for the facility's discharge.

SPECIFIC COMMENTS

<u>Comment 4, Executive Summary, page iv.</u> For clarification purposes, we recommend that the second to last sentence in the second paragraph within the draft report's executive summary which states:

"The EC₅₀ was determined for side by side biomonitoring tests using river water for the dilution water in one test, the site water sample, and moderately hard laboratory water for the dilution water in the second test"

be revised to state.

"The EC₅₀ was determined for side by side biomonitoring tests using site water in one test and moderately hard laboratory water in the second test. The site water was simulated downstream-water consisting of 92 parts effluent and 8 parts upstream river water."

Comment 5, Executive Summary, page iv. It appears that an opening parenthesis "(" should be added to the beginning of the following phrase found within the first sentence in the fourth paragraph of the executive summary: "the mean EC_{50} from a large number of published toxicity tests with laboratory water, and provided in the guidance document)."

<u>Comment 6, Executive Summary, page v.</u> We recommend that the following revision (shown in underline/strikeout format) be incorporated into the third sentence found within the fourth paragraph of the executive summary: "For both study events, the SMAV EC₅₀ was used for in place of the laboratory EC₅₀."

Comment 7, Section 2-Field Sample Collection, Table 2-1. Footnote #3 associated with Table 2-1 states that precipitation total for the second WER study event is for January 31, 2007, to February 13, 2007. However, it appears that the precipitation total of 1.61 inches for the second study event includes rainfall that occurred on February 14, 2007, as well. Therefore, we recommend that the February 13, 2007, date in footnote #3 be revised to February 14, 2007.

Comment 8, Section 4-Results, January 2007 Study Event, "Effluent Chemical Parameters," page 4-1, and Tables 4-4 and 4-5. The first sentence in the second paragraph under the subheading "Effluent Chemical Parameters" states, "Effluent flow on the day of the study was recorded as 0.227 mgd..." However, the information in Tables 4-4 and 4-5 records an effluent flow of 0.56 mgd during the first WER study event. It is not clear which flow value is the correct one. Please ensure that the correct effluent flow value is reflected in both the text and tables within Section 4 of the report.

Comment 9, Section 4-Results, January 2007 Study Event, "Effluent Chemical Parameters," pages 4-1 and 4-2. The second sentence in the second paragraph under the subheading "Effluent Chemical Parameters" states, "The total recoverable copper concentration was reported as 6.5 μg/L..." However, information from the lab report provided in Appendix 2 of the draft WER study report shows that 6.5 μg/L reflects the dissolved copper concentration. The total copper concentration is reported in the lab report as 17 μg/L. Therefore, we recommend that "6.5 μg/L" be replaced with "17 μg/L" in this sentence. Likewise, the first sentence in the third paragraph under the same subheading states, "The calculated load of TR copper in the sample collected from the effluent was 0.03 lb/day..." We recommend that "0.03 lb/day" be replaced with "0.08 lbs/day" to reflect the total copper load (instead of dissolved).

Comment 10, Section 4-Results, January 2007 Study Event, "Biomonitoring Tests and WER," pages 4-2 to 4-3. For clarification purposes, we recommend that the first sentence in the first paragraph under the "Biomonitoring Tests and WER" subheading which states:

"The EC₅₀ was determined for side by side biomonitoring tests using river water for the dilution water in one test and moderately hard laboratory water for the dilution water in the second test"

be revised to state,

"The EC₅₀ was determined for side by side biomonitoring tests using site water in one test and moderately hard laboratory water in the second test. The site water was simulated downstream-water consisting of 92 parts effluent and 8 parts upstream river water."

Comment 11, Section 4-Results, January 2007 Study Event, "Biomonitoring Tests and WER," pages 4-2 to 4-3. The third sentence in the first paragraph under the "Biomonitoring Tests and WER" subheading states, "As presented in the laboratory report and update report provided in Appendix 2, the EC₅₀ was calculated as 45.26 μ g/L TR copper for the Site Water (92 percent effluent/8 percent river water) and <6.5 μ g/L TR copper for the laboratory waters."

- a. From the information provided in Appendix 2, EPA believes that the two uses of the acronym for total recoverable ("TR") in the above sentence should be replaced with the word "dissolved."
- b. EPA noted that different methods were utilized in the first study event for selecting the copper concentrations to be used in determining EC₅₀ values for the site water and

laboratory water. For example, the site water dissolved copper EC $_{50}$ of 45.26 µg/L appears to have been derived using dissolved copper concentrations measured at the end of the 48-hour test, whereas the laboratory water dissolved copper EC $_{50}$ of <6.5 appears to have been derived using the nominal concentration, rather than a measured dissolved concentration. EPA recommends that consistent methods be utilized in selecting the copper concentrations to be used in determining EC $_{50}$ values for the site water and laboratory water. Further, EPA's 1994 interim WER guidance (see page 59) recommends the use of the time-weighted average measured concentrations in determining EC $_{50}$ values. We recommend that this approach also be utilized in this WER study. As shown in the summary table presented in comment #20 below, EPA calculated a site water dissolved EC $_{50}$ value of 46.69 µg/L and a laboratory water dissolved EC $_{50}$ values replace the values currently presented in the third sentence within the first paragraph under the "Biomonitoring Tests and WER" subheading.

Comment 12, Section 4-Results, January 2007 Study Event, "Biomonitoring Tests and WER," page 4-3. EPA recommends that the hardness normalization and WER calculations provided in the last three paragraphs under the subheading "Biomonitoring Tests and WER" for the first study event be revised to reflect incorporation of the dissolved EC₅₀ values recommended in comment #11(b) above. Utilizing the hardness normalized site water EC₅₀ and Species Mean Acute Value (SMAV), EPA derived a dissolved WER for the first study event of 11.8717. Please note that EPA's hardness normalization and WER calculations for the two study events can be found in the Excel file titled, "Two Bayou WER Study – Hardness Normalization Calculations.doc" attached in the email transmitting these comments on the draft report.

Comment 13, Section 4-Results, February 2007 Event, "Effluent Chemical Parameters," page $\underline{4-4}$. The second sentence in the second paragraph under the subheading "Effluent Chemical Parameters" states, "The total recoverable copper concentration was reported as less than the detection limit of 6 µg/L ..." However, information from the lab report provided in Appendix 2 of the draft WER study report shows that the less than 6 µg/L reflects the dissolved copper concentration. The total copper concentration is reported in the lab report as 9.9 µg/L. Therefore, we recommend that the phrase "less than the detection limit of 6 µg/L" be replaced with "9.9 µg/L" in this sentence. Likewise, the first sentence in the third paragraph under the same subheading states, "The calculated load of TR copper in the sample collected from the effluent was 0.04 lb/day..." We recommend that "0.04 lb/day" be replaced with "0.06 lbs/day" to reflect the total copper load (instead of dissolved).

<u>Comment 14, Section 4-Results, February 2007 Event, "Biomonitoring Tests and WER," page 4-5</u>. For clarification purposes, we recommend that the first sentence in the first paragraph under the "Biomonitoring Tests and WER" subheading which states:

"The EC₅₀ was determined for side by side biomonitoring tests using river water for the dilution water in one test and moderately hard laboratory water for the dilution water in the second test"

be revised to state,

"The EC₅₀ was determined for side by side biomonitoring tests using site water in one test and moderately hard laboratory water in the second test. The site water was simulated downstream-water consisting of 92 parts effluent and 8 parts upstream river water."

Comment 15, Section 4-Results, February 2007 Event, "Biomonitoring Tests and WER," page $\underline{4-5}$. The third sentence in the first paragraph under the "Biomonitoring Tests and WER" subheading states, "As presented in the laboratory report and update report provided in Appendix 2, the EC₅₀ was calculated as 66.39 μ g/L TR copper for the site water and 5.565 μ g/L TR copper for the laboratory water."

- a. From the information provided in Appendix 2, EPA believes that the two uses of the acronym for total recoverable ("TR") in the above sentence should be replaced with the word "dissolved."
- b. The site water and laboratory water dissolved copper EC $_{50}$ s of 66.39 µg/L and 5.565 µg/L appear to have been derived using dissolved copper concentrations measured at the beginning of the 48-hour test. EPA's 1994 interim WER guidance (see page 59) recommends the use of the time-weighted average measured concentrations in determining EC $_{50}$ values. We recommend that this approach also be utilized in this WER study. As shown in the summary table presented in comment #20 below, EPA calculated a site water dissolved EC $_{50}$ value of 65.64 µg/L and a laboratory water dissolved EC $_{50}$ value of 5.15 µg/L for the second WER study event. We recommend that these EC $_{50}$ values replace the values currently presented in the third sentence within the first paragraph under the "Biomonitoring Tests and WER" subheading.

Comment 16, Section 4-Results, February 2007 Event, "Biomonitoring Tests and WER," page 4-6. EPA recommends that the hardness normalization and WER calculations provided in the last three paragraphs under the subheading "Biomonitoring Tests and WER" for the second study event be revised to reflect incorporation of the dissolved EC₅₀ values recommended in comment #15(b) above. Utilizing the hardness normalized site water EC₅₀ and SMAV, EPA derived a dissolved WER for the second study event of 20.2966. Please note that EPA's hardness normalization and WER calculations for the two study events can be found in the Excel file titled, "Two Bayou WER Study – Hardness Normalization Calculations.doc" attached in the email transmitting these comments on the draft report.

Comment 17, Section 4-Results, January 2007 Study Event and February 14, 2007 Study Event, "Biomonitoring Tests and WER," pages 4-3 and 4-5 to 4-6. From the draft report, it appears that the dissolved WERs from the two study events were selected for use in deriving the final WER rather than the total WERs. While it is certainly acceptable and necessary to choose either a dissolved or total final WER for use in developing site-specific copper criteria, EPA recommends that:

a. total copper EC_{50} values for site water and laboratory water for both WER study events also be reported and summarized within these subsections of Section 4, along with the hardness normalization calculations and total WERs;

b. the decision to utilize only the individual dissolved WERs (as opposed to the individual total WERs) in deriving the final WER can be discussed under the subheading "Final Site WER and Criteria;" and,

c. the subheading "Final Site WER and Criteria" also be revised to reflect EPA's previous recommendation (see comment #3 above) that the final WER be based only upon the WER determined from the first WER study event (final dissolved WER = 11.8717).

Comment 18, Section 4-Results, Tables 4-3, 4-4, and 4-5. From the information provided in Appendix 2 of the draft report, EPA believes that the cell in each of these three tables which currently states, "Copper, total recoverable," should be revised to "Copper, dissolved."

<u>Comment 19, Section 4-Results.</u> EPA recommends that the following two tables, which incorporate relevant data included within Appendix 2, also be included in the draft report following Table 4-5.

Table 4- . ANALYTICAL RESULTS FOR LABORATORY WATER Shumaker Public Service Corporation, East Camden, Arkansas

Compound	Units	EVENT 1 January 3, 2007	EVENT 2 February 14, 2007		
Alkalinity	mg/L (as CaCO3)	56	58		
TSS	mg/L	<4	<4		
pН	units	7.4	8		
Hardness	mg/L	77	79		
DOC	mg/L	<1	<1		

Table 4- . ANALYTICAL RESULTS FOR SIMULATED DOWNSTREAM WATER Shumaker Public Service Corporation, East Camden, Arkansas

Compound	Units	EVENT 1 January 3, 2007	EVENT 2 February 14, 2007		
Alkalinity	mg/L (as CaCO3)	16	14		
TSS	mg/L	8	16		
pН	units	6.7	7.2		
Hardness	mg/L	16	13		
DOC	mg/L	7.6	8.8		

<u>Comment 20, Section 4-Results.</u> EPA recommends that the following two WER study event summary tables¹ also be included in the draft report following the two new tables presented in comment #19 above:

¹ Please note that these recommended new tables are also provided in the Excel file titled, "Two Bayou WER Study Summary Tables.doc" attached in the email transmitting these comments on the draft report.

Shumaker Public Service Corporation (NPDES No. AR0034363) East Camden, Arkansas Two Bayou WER Study Event 1 - January 3, 2007

Laboratory Water Test (Hardness = 77)

Nominal Cu (μg/L)	Measured Total Cu (pre-test) (μg/L)	Measured Total Cu (post- test) (µg/L)	Time- Weighted Average (Total, μg/L)	% Loss	Measured Dissolved Cu (pre- test) (μg/L)	Measured Dissolved Cu (post- test) (μg/L)	Time- Weighted Average (Dissolved, μg/L)	% Loss	Mortality (n = 20)	EC ₅₀ (μg/L)
Control	1	1	1	0.00	1	1	1	0.00	0	
6.5	7	7.3	7.15	-0.04	6.3	5.7	6	0.10	19	Total = <7.15
11	10	11	10.5	-0.10	10	9.3	9.65	0.07	20	
18	17	16	16.5	0.06	17	17	17	0.00	20	
30	29	31	30	-0.07	28	30	29	-0.07	20	Dissolved = <6
50	49	50	49.5	-0.02	47	48	47.5	-0.02	20	

^{*}Note - Lab water control copper concentrations (total and dissolved) were below the detection limit of 1 µg/L.

Simulated Downstream Water Test (Hardness = 16)

Nominal Cu (μg/L)	Measured Total Cu (pre-test) (μg/L)	Measured Total Cu (post- test) (µg/L)	Time- Weighted Average (Total, μg/L)	% Loss	Measured Dissolved Cu (pre- test) (μg/L)	Measured Dissolved Cu (post- test) (μg/L)	Time- Weighted Average (Dissolved, μg/L)	% Loss	Mortality (n = 20)	EC ₅₀ (μg/L)
Control	11	4.9	7.95	0.55	8.5	2.8	5.65	0.67	0	
20	27	20	23.5	0.26	18	18	18	0.00	0	Total = 66.26
40	47	44	45.5	0.06	34	29	31.5	0.15	0	
60	66	61	63.5	0.08	45	42	43.5	0.07	5	
80	83	76	79.5	0.08	59	58	58.5	0.02	20	Dissolved = 46.69
100	110	110	110	0.00	78	84	81	-0.08	20	

Shumaker Public Service Corporation (NPDES No. AR0034363) East Camden, Arkansas Two Bayou WER Study Event 2 – February 14, 2007

Laboratory Water Test (Hardness = 79)

Nominal Cu (μg/L)	Measured Total Cu (pre-test) (μg/L)	Measured Total Cu (post- test) (µg/L)	Time- Weighted Average (Total, μg/L)	% Loss	Measured Dissolved Cu (pre- test) (μg/L)	Measured Dissolved Cu (post- test) (μg/L)	Time- Weighted Average (Dissolved, μg/L)	% Loss	Mortality (n = 20)	EC ₅₀ (μg/L)
Control	1	1	1	0.00	1	1	1	0.00	0	
2.5	3.1	2.5	2.8	0.19	3	1.9	2.45	0.37	0	Total = 5.69
5	5.3	5.3	5.3	0.00	5	4.5	4.75	0.10	11	
10	11	12	11.5	-0.09	11	11	11	0.00	18	
20	21	24	22.5	-0.14	19	23	21	-0.21	20	Dissolved = 5.15
40	40	49	44.5	-0.23	41	48	44.5	-0.17	20	

^{*}Note - Lab water control copper concentrations (total and dissolved) were below the detection limit of 1 µg/L.

Simulated Downstream Water Test (Hardness = 13)

Nominal Cu (μg/L)	Measured Total Cu (pre-test) (μg/L)	Measured Total Cu (post- test) (µg/L)	Time- Weighted Average (Total, μg/L)	% Loss	Measured Dissolved Cu (pre- test) (μg/L)	Measured Dissolved Cu (post- test) (μg/L)	Time- Weighted Average (Dissolved, µg/L)	% Loss	Mortality (n = 20)	EC ₅₀ (μg/L)
Control	8.8	6.2	7.5	0.30	5.7	5.6	5.65	0.02	0	
20	32	24	28	0.25	20	20	20	0.00	0	Total = 85.91
40	50	38	44	0.24	34	33	33.5	0.03	0	
60	66	48	57	0.27	47	47	47	0.00	0	
80	89	73	81	0.18	62	61	61.5	0.02	7	Dissolved = 65.64
100	110	97	103.5	0.12	80	77	78.5	0.04	17	

Comment 21, Section 5-Conclusions, pages 5-1 to 5-2. EPA recommends that Section 5 be revised to reflect EPA's previous recommendation (see comment #3 above) that the final WER be based only upon the WER determined from the first WER study event (final dissolved WER = 11.8717). Please note that the table in both Section 5 and the Executive Summary (on page v) which shows the final dissolved WER and revised site-specific copper criteria should also be revised to reflect this recommendation.

Comment 22, Appendix 2. Please include a table within Appendix 2 which describes the dissolved oxygen, pH, and temperature measurements taken during the four 48-hour toxicity tests (both test events and both laboratory and site water tests (total = 4)). Page 3-2 of the draft WER report states that these measurements were taken; however, the toxicity test record sheets in Appendix 2 do not currently provide this information. It is important to provide a record showing that dissolved oxygen, pH, and temperature levels remained acceptable throughout the toxicity testing.